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Title: **EP0799808A1: Semiconducting ceramic compounds having negative resistance-temperature characteristics with critical temperatures**[Gerr

Derwent Title: Semiconducting ceramic compound - comprises rare earth transition element oxide and has negative resistance temperature characteristics and critical temperatures [Derwent Record]

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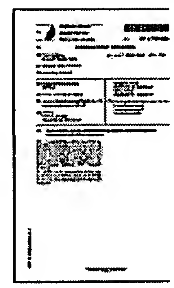

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Abstract: A semiconducting ceramic compound has negative resistance-temperature characteristics with a critical temperature and consists essentially of a rare-earth transition element oxide which is SmNiO3. Samarium contained in SmNiO3 may be partially replaced by a group of elements selected from praseodymium, neodymium, europium, gadolinium, yttrium, dysprosium and bismuth. The resistivity of this semiconducting ceramic compound sharply drops beyond a specific critical temperature and such critical temperature can be freely set to a desired level.

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Family: Show known family members (at least 5)

Description: Expand full description

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First Claim: Show all claims

1. A semiconducting ceramic compound having negative resistance-temperature characteristics with a critical temperature, said compound consisting essentially of a rare-earth transition element oxide, characterized in that said rare-earth transition element oxide is $SmNiO_3$.

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(54) Semiconducting ceramic compounds having negative resistance-temperature characteristics with critical temperatures

(57) A semiconducting ceramic compound has negative resistance-temperature characteristics with a critical temperature and consists essentially of a rare-earth transition element oxide which is $SmNiO_3$. Samarium contained in $SmNiO_3$ may be partially replaced by a group of elements selected from praseodymium, neodymium, europium, gadolinium, yttrium, dysprosium and bismuth.
The resistivity of this semiconducting ceramic compound sharply drops beyond a specific critical temperature and such critical temperature can be freely set to a desired level.

EP 0 799 808 A1

Description

BACKGROUND OF THE INVENTION

The present invention relates to a semiconducting ceramic compound having negative resistance-temperature characteristics with a critical temperature, the compound consisting essentially of a rare-earth transition element oxide.

Negative temperature coefficient semiconducting ceramics (hereinafter referred to as NTC ceramics) whose electrical resistance is high at room temperature and drops with temperature increase are known in the prior art. Examples of materials for producing such NTC ceramics are oxides of transition elements which have a spinel crystalline structure and mainly contain a few elements selected from aluminum, manganese, iron, nickel, cobalt and copper, as well as cobalt-containing rare-earth oxides which have a perovskite crystalline structure and mainly contain $LaCoO_3$.

NTC ceramic devices produced by forming electrodes on each piece of an NTC ceramic material consisting essentially of the oxides of some of the aforementioned transition elements are used as rush current preventing devices for switching regulators or for the protection of motors or halogen lamps, or as temperature-sensitive devices for temperature sensing or for detecting the surface of a liquid, for instance. On the other hand, NTC ceramic devices produced by forming electrodes on each piece of an NTC ceramic material consisting essentially of a cobalt-containing rare-earth oxide are commonly used as rush current preventing devices for switching regulators or for the protection of motors or halogen lamps, for instance.

Also known in the prior art are critical temperature resistor semiconducting ceramics (hereinafter referred to as CTR ceramics) whose electrical resistance sharply drops beyond specific temperatures. Examples of materials for producing such CTR ceramics are vanadium dioxide (VO_2) and nickel-containing rare-earth oxides, the latter including $SmNiO_3$, $NdNiO_3$, $PrNiO_3$ and $EuNiO_3$, for instance.

CTR ceramic devices produced by forming electrodes on each piece of a CTR ceramic material consisting essentially of VO_2 are used as temperature-sensing devices for fire-alarm systems.

Although the aforementioned NTC ceramics composed essentially of the oxides of some of the transition elements and the NTC ceramics consisting essentially of the cobalt-containing rare-earth oxides have negative resistance-temperature characteristics, neither of them exhibit critical temperatures at which their resistance sharply drops. It has therefore been necessary to use the conventional NTC ceramic devices together with a controlling microcomputer circuit when applying them to switching on-off operations, and this has resulted in large component sizes and high costs of materials.

While the CTR ceramics consisting essentially of VO_2 have such characteristics that their resistivity drops from 10^4 ohm-centimeters to 10 ohm-centimeters in a temperature range of 60°C to 80°C, they are not in a stable phase at room temperature. This develops a problem that these CTR ceramics can be destroyed when brought into contact with air or moisture. Furthermore, since their critical temperatures are restricted within the range of 60°C to 80°C, their applications are limited to temperature-sensing devices for fire-alarm systems.

The resistance of the CTR ceramics consisting essentially of the aforementioned nickel-containing rare-earth oxides sharply drops beyond specific temperatures (metal-to-semiconductor phase transition temperatures) as discussed in a paper presented by J.B. Torrance, et al. (FIGS. 1 and 2 on page 8,210 of Physical Review B45 [14], 1990) Such characteristics of the CTR ceramics, particularly $SmNiO_3$, $NdNiO_3$ and $PrNiO_3$, are also discussed in a paper presented by P. Lacorre, et al. (FIG. 4 on page 225 of Solid State Chemistry, 1991)

Although these papers give resistance values of different samples in ohms at about their phase transition temperatures, neither of them indicates specific shapes of the samples. It is therefore impossible to know their resistivities or conductivities, especially at room temperature (25°C), from the papers. The inventor of the present invention analyzed the crystalline structures of the same samples by using the X-ray diffraction method and succeeded in identitying $NdNiO_3$ and $PrNiO_3$ in the samples. An analysis of the sample containing $SmNiO_3$ revealed a diffraction pattern seemingly produced by $SmNiO_3$, but there was found a diffraction pattern of NiO as well. Therefore, it was impossible to determine that the CTR characteristics of that sample was caused by $SmNiO_3$ alone.

Substituting lanthanum (La) for 30% of neodymium (Nd) contained in $NdNiO_3$ reduces its phase transition temperature from -70°C to -170°C as discussed in a paper presented by J.B. Garcia-Munoz, et al. (FIG. 1 on page 15, 198 of Physical Review B5 [21], 1995) However, it is not certain whether the phase transition temperature can be altered by substituting a rare-earth element, rather than lanthanum (La), for neodymium (Nd).

SUMMARY OF THE INVENTION

It is an object of the invention to provide semiconducting ceramic compounds having negative resistance-temperature characteristics, wherein their resistivity sharply drops beyond specific critical temperatures and such temperatures can be freely set to a desired level.

The invention provides a semiconducting ceramic compound of above mentioned kind, which is characterized in that said rare-earth transition element oxide is $SmNiO_3$.

In the above semiconducting ceramic compound, samarium contained in $SmNiO_3$ may be partially replaced by a group of elements selected from praseodymium, neodymium, europium, gadolinium, yttrium, dysprosium and bismuth.

It is preferred that a molar ratio of samarium to nickel in the above semiconducting ceramic compound is between 0.80 and 1.05.

The invention also provides a rush current preventing device for use with the above described semiconducting ceramic compounds.

The invention also provides a soft-start control device for a motor for use with the above described semiconducting ceramic compounds.

The invention also provides a temperature-sensing device for use with the above described semiconducting ceramic compounds.

The semiconducting ceramic compound of the invention has negative resistance-temperature characteristics, wherein the resistivity of the compound is large below a phase transition temperature and sharply drops beyond that phase transition (or critical) temperature. This semiconducting ceramic compound exhibits a large difference in electrical resistance between its energized and non-energized conditions.

The semiconducting ceramic compound of the invention exhibits negative resistance-temperature characteristics with its resistance sharply decreasing in a temperature range between 100°C and 140°C. Accordingly, a device constructed with this semiconducting ceramic compound can be used with least influence of environmental and operating conditions.

The semiconducting ceramic compound of the invention can be used to produce rush current preventing devices for switching regulators or for the protection of motors or halogen lamps, soft-start control devices for motors, or temperature-sensitive devices for temperature sensing, liquid surface detection, overheat prevention or for fire-alarm systems.

Furthermore, the phase transition temperature can be set to a desired value by completely or partially replacing samarium contained in $SmNiO_3$ with neodymium or gadolinium, making the compound even more suited to liquid surface detection and temperature-sensing applications.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph showing resistance-temperature characteristics of semiconducting ceramic devices according to first and second embodiments of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIRST EMBODIMENT

A powdered compound containing nickel (Ni), such as Ni_2O_3, NiO or Ni(OH), a powdered compound containing samarium (Sm), such as Sm_2O_3 or $Sm(OH)_3$, and a powdered compound containing neodymium (Nd), such as Nd_2O_3 or $Nd(OH)_3$ were weighed and mixed so that a molar ratio of the sum of samarium and neodymium to nickel ((Sm+Nd)/Ni) becomes 0.98, and thereby the chemical formula $(Sm_{1-x}Nd_x)_{0.98}NiO_3$ is satisfied after a later sintering process. This mixture was blended and pulverized in a ball mill through a 24-hour wet milling process, mixed with a binder, and further blended in the ball mill for another one hour. The resultant compound was filtered, dried, and press-molded at a pressure of 2 t/cm^2. This semifinished molded product was sintered in oxygen which was maintained at a temperature of 900°C for a period of two hours to eliminate the binder, and then in a hot isostatic pressing (HIP) furnace containing oxygen which was maintained at a temperature of 1000°C and a pressure of 2000 bars for a period of four hours to eventually obtain a disklike sintered product measuring 9 mm in diameter and 3 mm in thickness. External electrodes composed of silver were formed on both sides of this sintered product by a vacuum evaporation method to complete a semiconducting ceramic device.

Samples of semiconducting ceramic devices thus obtained were subjected to various measurements to evaluate their characteristics. More specifically, temperatures (Tc) at which the temperature coefficient of resistance changes from a negative value to a positive value, temperature-dependent changes in resistance (ψ), and resistivities (ρ) at different temperatures were measured, and measurement results are shown in Table 1. Since the temperature at which the temperature coefficient of resistance of each sample begins to sharply drop is difficult to identify, its temperature-dependent change in resistance (ψ) is expressed by the following formula:

$$\psi = \log_{10}\{R(Tc - 50)/R(Tc)\}$$

Table 1

Amount of substitution x	Tc (°C)	ψ	ρ (Tc) (Ωcm)	ρ (25°C) (Ωcm)
0.0	134	2.04	0.00026	0.18
0.1	114	2.14	0.00022	0.12
0.2	94	2.20	0.00019	0.070
0.3	74	2.22	0.00018	0.042
0.4	54	2.26	0.00017	0.019
0.5	34	2.31	0.00015	0.020
0.6	14	2.31	0.00014	0.00019
0.7	-4	2.40	0.00010	0.00024
0.8	-24	2.37	0.00012	0.00038
0.9	-44	2.40	0.00012	0.00052
1.0	-62	2.44	0.00011	0.00063

SECOND EMBODIMENT

A powdered compound containing nickel (Ni), such as Ni_2O_3, NiO or Ni(OH), a powdered compound containing samarium (Sm), such as Sm_2O_3 or $Sm(OH)_3$, and a powdered compound containing gadolinium (Gd), such as Gd_2O_3 or $Gd(OH)_3$ were weighed and mixed so that a molar ratio of the sum of samarium and gadolinium to nickel ((Sm+Gd)/Ni) becomes 0.98, and thereby the chemical formula $(Sm_{1-y}Gd_y)_{0.98}NiO_3$ is satisfied after a later sintering process. Several samples of semiconducting ceramic devices were obtained from this mixture using the same production method as used in the first embodiment.

These semiconducting ceramic devices were subjected to various measurements to evaluate their characteristics in the same manner as the first embodiment, and measurement results are shown in Table 2.

Table 2

Amount of substitution x	Tc (°C)	ψ	ρ (Tc) (Ωcm)	ρ (25°C) (Ωcm)
0.0	134	2.04	0.00026	0.18
0.1	154	2.04	0.00028	0.25
0.2	174	2.00	0.00031	0.32
0.3	194	1.95	0.00035	0.37
0.4	214	1.92	0.00038	0.41
0.5	234	1.89	0.00041	0.46
0.6	254	1.85	0.00045	0.51
0.7	274	1.82	0.00048	0.55
0.8	294	1.79	0.00051	0.59
0.9	314	1.79	0.00051	0.63
1.0	334	1.74	0.00057	0.67

FIG. 1 is a graph showing resistance-temperature characteristics of the semiconducting ceramic devices obtained in the first and second embodiments described above. It can be seen from this Figure that nickel-containing rare-earth

oxides of the embodiments exhibit negative resistance-temperature characteristics with critical temperatures.

The aforementioned semiconducting ceramic materials $(Sm_{1-x}Nd_x)_{0.98}NiO_3$ and $(Sm_{1-y}Gd_y)_{0.98}NiO_3$ exhibit negative temperature coefficients below their phase transition temperatures, and positive temperature coefficients beyond their phase transition temperatures. With these nickel-containing rare-earth oxides (composed of rare-earth elements and NiO_3), it is possible to obtain a desired phase transition temperature by choosing a proper mixing ratio of the individual rare-earth elements.

In particular, $Sm_{0.98}NiO_3$ and those ceramic materials which are produced by partially substituting neodymium (Nd) for samarium (Sm) contained in $Sm_{0.98}NiO_3$ exhibit far superior characteristics, compared to the conventionally known ceramic materials, when used in rush current preventing devices, soft-start control devices for motors, or temperature-sensing devices. The rush current preventing effect of $Sm_{0.98}NiO_3$, for example, does not decrease so much even when switching on-off operations are repeated because its resistance varies by a factor of over 100 between 100°C and 140°C.

Since $Sm_{0.98}NiO_3$ has a B constant of 1400K at 25°C, which is lower than that of conventional thermistors used for preventing rush current, it is possible to reduce variations of the rush current preventing effect caused by temperature changes in equipment between -50°C and 50°C.

Moreover, a device formed from $Sm_{0.98}NiO_3$ may be kept in air without sealing because the material is stable even at room temperature.

The molar ratio of the sum of rare-earth elements to nickel is not limited to 0.98, but may take other values chosen between 0.80 and 1.05. Also, the molar ratio of samarium to nickel is not limited to 0.98, but may be set to 1.00, for example.

If it is desired to reduce the phase transition temperature of $SmNiO_3$, samarium contained in it should be completely or partially replaced not only with neodymium but also with praseodymium (Pr) or lanthanum (La). On the contrary, if it is desired to increase its phase transition temperature, samarium contained in it should be completely or partially replaced not only with gadolinium but also with europium (Eu), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y) and bismuth (Bi). It is to be noted, however, that a technique of partial substitution by lanthanum is known in the prior art and is not included in this invention.

Although the semiconducting ceramic materials of the foregoing embodiments were obtained by sintering in the HIP furnace, such ceramic products may be obtained by using a single crystal growth process, or a thick-film or thin-film forming process instead of the sintering process. Furthermore, the HIP furnace is not absolutely necessary for the production of those semiconducting ceramic materials. Alternative techniques usable for their production include such synthesis methods as a hydrothermal synthesis method, sol-gel method, atomized thermal decomposition method, and chemical vapor deposition (CVD) method. The sintering atmosphere may be filled with ozone, or an oxidizer, such as hydrogen peroxide, may be added to raw materials when they are being mixed so that the oxygen content of the sintering atmosphere becomes excessive .

While the invention has been described with reference to the disklike semiconducting ceramic devices in foregoing embodiments, the invention is not necessarily limited to that shape of devices but may be applied to other types, and forms, of semiconducting ceramic devices, which include multilayered devices, cylindrical-shaped devices, and square-chip devices, for example. According to the aforementioned embodiments, the electrodes of the semiconducting ceramic devices were formed on their external surfaces. In a modified form of the invention, electrodes may be formed inside each of the semiconducting ceramic devices.

Although the electrodes were formed from silver in the aforementioned embodiments, other electrode materials, such as palladium, platinum, nickel, copper, chromium, an alloy containing silver, and an alloy thereof, can be used without changing electrical characteristics of the individual devices. Furthermore, the electrode-forming method is not limited to vacuum evaporation. Other methods usable for producing the electrodes include thin-film technology such as sputtering, electroless plating, and thick-film forming techniques such as plating and printing.

Claims

1. A semiconducting ceramic compound having negative resistance-temperature characteristics with a critical temperature, said compound consisting essentially of a rare-earth transition element oxide, characterized in that said rare-earth transition element oxide is $SmNiO_3$.

2. A semiconducting ceramic compound according to claim 1, characterized in that
samarium contained in $SmNiO_3$ is partially replaced by a group of elements selected from praseodymium, neodymium, europium, gadolinium, yttrium, dysprosium and bismuth.

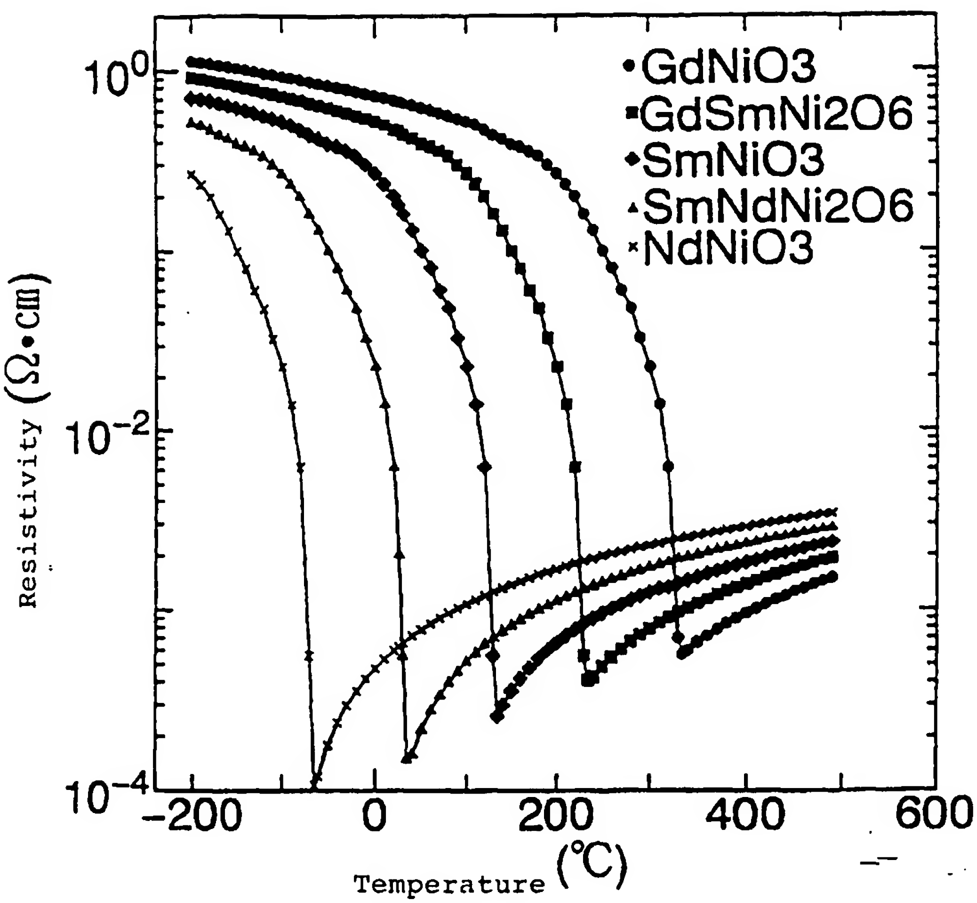
3. A semiconducting ceramic compound according to claim 1 or 2, characterized in that
a molar ratio of samarium to nickel is between 0.80 and 1.05.

4. A rush current preventing device for use with the semiconducting ceramic compound according to one of Claims 1 to 4.

5. A soft-start control device for a motor for use with the semiconducting ceramic compound according to one of Claims 1 to 4.

6. A temperature-sensing device for use with the semiconducting ceramic compound according to one of Claims 1 to 4.

Fig. 1



GdNiO3
GdSmNi2O6
SmNiO3
SmNdNi2O6
NdNiO3
Resistivity (Ω•cm)
10^0
10^-2
10^-4
-200
0
200
400
600
Temperature (℃)

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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 4307

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 609 888 A (MURATA MANUFACTURING CO., LTD.) * page 3, line 57 - page 4, line 38; claims 1,2,4,8,9; example 3; table 5 * ---	1,4-6	C04B35/50 H01C7/04
X,D	PHYSICAL REVIEW B, vol. 45, no. 14, 1 April 1992, pages 8209-8212, XP002035291 P. LACORRE ET AL.: * page 8209; figure 1 * ---	1-3	
X,D	JOURNAL OF SOLID STATE CHEMISTRY, vol. 91, 1991, pages 225-237, XP002035292 P. LACORRE ET AL.: * page 225 - page 227 * -----	1,3	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C04B H01C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 July 1997	Luethe, H

CATEGORY OF CITED DOCUMENTS

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